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# EVALUATION OF NEW BRUNSWICK SHALE OIL FOR ITS POTENTIAL AS AN ASPHALT FEEDSTOCK

by

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Hon. Morris Green, Minister

1989

# EVALUATION OF NEW BRUNSWICK SHALE OIL

# FOR ITS POTENTIAL AS AN ASPHALT FEEDSTOCK

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January 10, 1989

New Brunswick Department of Natural Resources
and Energy
Energy Branch
P.O. Box 6000
Fredericton, New Brunswick
E3B 5H1

Attention: C. St. Peter
Senior Geologist

**RE: Evaluation of New Brunswick Shale Oil for its Potential as an Asphalt Feedstock: Report 8737-1**

Dear Clinton:

I am pleased to submit one unbound copy and three bound copies of this report. As you are aware, there is some interest in this subject in Canada and it is being actively pursued in the United States. Dr. M.F. Wilson, Research Scientist with the Energy Research Laboratories of the Canada Centre for Mineral and Energy Technology in Ottawa has suggested that CANMET might consider sponsoring a symposium on the subject given interest at the provincial level. I believe that this possibility should be actively pursued. The current interest in highway construction in New Brunswick is timely and suggests that the necessary broad interest in the potential of shale oil modified asphalts maybe generated through the use of this report and possibly a federal-provincial-industry symposium.

I am available to discuss the report and related subjects at your convenience.

Yours truly,

THREE-D GEOCONSULTANTS LIMITED

F.D. Ball
Senior Geologist

## SUMMARY

There is a trend in oil refining to process the bottom end of the crude oil barrel into lighter distillates and transportation fuels, at the expense of producing petroleum binders for asphalt. In addition, given the fluctuations in world crude oil markets of the past decade and a half, sources of refinery feedstock are not necessarily fixed with the result that crude oil characteristics and resultant asphalt properties vary. These factors have been identified as being major contributors to an increasing number of road pavement problems. These problems are exacerbated by the significant increases in traffic volumes and increased truck weights in recent years and the advanced age of the North American highways system.

In the United States, sectors of the oil shale industry have recognized the market potential for shale oils in asphalt production. Research suggests that shale-oil-based asphalts enhance pavement durability. Evidence indicates that basic, probably pyridinic, nitrogen compounds are responsible for the observed increased moisture resistance of shale-oil-derived asphaltic concretes. In addition, it has been found that nitrogen-bearing additives derived from both shale oil and from coal liquids enhance pavement flexibility and durability upon recycling. Western U.S. shale oil asphalts, however, are susceptible to oxidative hardening, a feature detrimental to pavement durability. Blends of petroleum asphalts and up to 20% shale oil asphalt show no abnormal susceptibility to oxidative hardening but do exhibit improved resistance to moisture damage.

Shale oils derived from the Albert Formation in New Brunswick are nitrogen bearing but no information exists indicating their content of the various types of nitrogen compounds. The use of New Brunswick shale oil as a feedstock for the production of asphalt to be blended with conventional petroleum asphalts or for the production of asphalt recycling agents is worthy of further

consideration. Such products would not compete directly with conventional oil and gas as a fuel and could command, due to enhanced performance, a higher market demand in preference to competing conventional crude-derived asphalt products. Production of such products would therefore buffer the economics of producing shale oil against the full brunt of the downside of conventional crude oil markets. To this end a program of further work is recommended. A suitably sized sample of New Brunswick shale oil must be acquired, analyzed and distilled to yield a sample of asphalt. The shale oil asphalt can then be blended and the appropriate tests conducted to determine whether New Brunswick shale oil asphalts possess enhanced durability characteristics.

## Résumé

L'industrie du raffinage a tendance à traiter le fond des barils d'huile brute pour les transformer en produits distillés plus léger et en huiles de transport, au lieu de produire des produits pour lier l'asphalte. En plus, due aux fluctuations sur le marché de l'huile brute durant la dernière décénie et demi, les sources d'approrisionement pour les raffineries ne sont pas constantes, ceci résultant en des caracteristiques variables pour l'huile brute et l'asphalte produite. Ces facteurs furent identifiés comme étant des contributeurs importants au nombre croissant de problèmes des routes pavées. Ces problèmes devienent encore plus importants si on tient compte de l'augmentation de l'intensité du trafic et du poids des camions sur les autoroutes d'âge relativement avancé de l'Amerique du Nord.

Au Etats-Unis, le secteur des schistes bitumineux reconait le potentiel du marché de ces huiles de schistes dans la production d'asphalte. Des recherches sur le sujet attestent de la durabilité accrue de l'asphalte fait à partire de schistes bitumineux. Ces recherches suggèrent que des produits d'azote de base, probablement pyridinic, seraient à l'origine de la plus grande résistance à l'humidité des produits d'asphalte utilisant des schistes bitumineux. En plus, les additifs contenant de l'azote, provenant des schistes bitumineux ou des liquides de charbon, auraient une plus grande flexibilité et seraient plus durable après avoir été reciclé. L'asphalte à base de schistes bitumineux de l'ouest des Etats-Unis tend à s'oxider, ce qui diminue la flexibilité du produit. Une combinaison d'asphalte à base de pétrole avec 20% d'asphalte à base de schistes bitumineux résout ce problème et accroit la resistence du produit à l'humidité.

Les schistes bitumineux provenant de la formation Albert, au Nouveau Brunswick, contiennent de l'azote, mais aucune

information est disponible sur les types de produits d'azote présents. L'utilisation des schistes bitumineux du Nouveau Brunswick comme produit de base dans la production d'asphalte destiné à être combiné avec de l'asphalte à base de pétrole, ou pour des produits utilisés dans le reciclage, devrait être considéré. Ces produits ne pouraient competitioner avec les sources conventionels de conburant, mais seraient possiblement compétitif sur le marché des produits d'asphalte. Cette methode protègerait l'huile produite à partir de schistes bitumineux contre les fluctuations des prix d'huile conventionnel. Pour ce faire, du travail additionel est recommendé. Un échantillon d'huile provenant de schistes bitumineux du Nouveau Brunswick devrait être obtenue, analysé et distillé pour produire un échantillon d'asphalte. Cet asphalte pourra être combiné avec de l'asphalte conventional et testé pour déterminer si l'asphalte produite à partir des schistes bitumineux du Nouveau Brunswick sera de plus grande durabilité.

## 1.0 INTRODUCTION

There has been an increasing trend in oil refining in recent years to process the bottom end of the crude oil barrel into lighter distillates and transportation fuels, at the expense of producing petroleum binders for asphalt. This recent and marked increase in "bottom of the barrel" processing has resulted in the alteration of the properties of resultant asphalts. In addition, given the fluctuations in the world crude oil market seen over the past decade and a half, sources of refinery feedstock are not necessarily fixed with the result that crude oil characteristics and resultant asphalt properties vary. These factors have been identified in the United States as being major contributors to an increasing number of road pavement problems. Discussions with officials of the New Brunswick Department of Transportation suggest that similar problems with asphalts have also been noted both in New Brunswick and across Canada. These problems are exacerbated by the significant increase in traffic volume and increased truck weights in recent years. The result in the United States has been a heightened concern for road construction and reconstruction, one aspect being the key role played by asphalt binders in pavement durability.

The economic impact of the use of asphalt binders in road construction is exemplified by the following statistics. Approximately 3.2 million kilometres, or 93% of all surfaced roads in the United States are paved with asphalt. The United States uses approximately 28 million tonnes of asphalt and asphalt-related paving materials annually and spends in excess of $19,000,000 (Can.) each year in the construction and maintenance of asphalt roadways. In addition, the Road Information Program in

Washington, D.C. reports that U.S. motorists spend in excess of $38,000,000,000 (Can.) annually in added vehicle operating costs due to rough and broken pavement. These figures can be put into a Canadian context by using the usual 10% factor to determine the cost to this country.

In the United States, sectors of the oil shale industry have recognized the market potential for shale oils in asphalt production. Research suggests that shale-oil-based asphalts enhance pavement durability. This research has been oriented towards investigating the causes, effects and thereby methods of mitigating moisture damage and binder embrittlement, the two principal failure mechanisms in asphalt pavements. Research has indicated that certain chemical compounds present in shale oil cause significant reduction in moisture damage when added to asphalt. The wear history of a 37 year old shale-oil-derived road near Rifle, Colorado supports these contentions. Samples of the pavement from this road have been collected for the purpose of analyses as part of the research.

In New Brunswick, it is the contention of all parties involved in oil shale development that multi-use of the resource is necessary for commercialization. The coal-oil shale fluidized bed cocombustion demonstration project underway in Chatham, New Brunswick (originally funded by the Federal Department of Energy, Mines and Resources and operated by the New Brunswick Electric Power Commission) is one step towards oil shale commercialization. In addition, a program is being undertaken by the New Brunswick Department of Natural Resources and Energy to characterize oil shale, oil shale ash and coal-oil shale ash. This program is aimed at full resource utilization through the development of a detailed understanding of the chemical and

physical properties of raw and spent oil shale. There is also a very real desire by several interested and informed parties to have a retort constructed as part of the demonstration facility at Chatham to complement the combustor. Bulk oil shale samples have, in fact, been acquired and are being used in pilot plant tests to evaluate various available retorting technologies.

An essential issue is whether shale oil can be produced in commercial quantities on an economically viable basis. To date, it has been assumed that the liquid products of oil shale production, be they either crude shale oil or syncrude, would be sold as refinery feedstocks or burner fuels, displacing conventional crude oils. The use of this product slate and intended market renders the economics of such shale oil projects totally dependent upon the competing crude oil markets. The underlying assumptions with regard to intended product slates and markets must be changed so as to shelter to some degree the costs of producing shale oil from the instability in conventional crude oil markets. This would require that a significant percentage of the products produced from a shale oil facility be converted into products that will command a higher market demand in preference to competing conventional oil. Specifically, it has been proposed that shale-oil-modified asphalt be produced. The product's demonstrated superior performance characteristics will create a demand and premium price in preference to asphalts derived solely from conventional crude oils. In Colorado, the New Paraho Corporation intends to produce sufficient quantities of shale oil to accommodate the controlled construction and evaluation of a one-mile test strip of shale-oil-modified asphalt pavement. The test strip will be constructed and evaluated in consultation with the Colorado State Department of Highways. In the same

vein, the U.S. Department of Energy and the State of Indiana have announced a jointly funded series of laboratory tests designed to confirm the enhanced durability of shale oil asphalts. If warranted, the U.S.D.O.E., the State and the New Paraho Corp. will embark upon a road test program and commercial feasibility study. The entire test and study program has been allocated a total budget of $4,500,000 (Can.).

These developments in oil shale utilization suggest that New Brunswick oil shales may offer similar development potential. This avenue warrants follow-up, particularly if the potential product will command a premium price removed from a direct economic link to crude oil.

## 2.0 ASPHALTS

Crude oil consists of different compounds or components that are mainly combinations of hydrogen and carbon atoms (hydrocarbons). Each of these compounds has its own boiling temperature. Generally, the more carbon atoms in the compound, the heavier the compound and the higher the boiling temperature. In specifying the character of crude oil, certain compounds are grouped into fractions that boil within the same temperature range. Crude oil compositions vary widely, the light crudes having more light hydrocarbon fractions whereas heavy crudes tend to have more heavy hydrocarbon fractions, including residue.

At the heavy end of crudes, are variable amounts of asphaltenes. Asphaltenes are polyaromatic compounds with high carbon to hydrogen ratios. The relatively high carbon content results from the way the aromatic rings are multiply bonded. When the asphaltene content is high enough, the material makes a good, strong, stable binder, that is, asphalt.

Asphalt is produced from the residue remaining after an asphaltic crude oil has been refined by the straight run method. The residue of a straight run (distilled) asphaltic crude, when vacuum flashed (fractionated at reduced pressure), will yield bottoms or residues that can be used directly as an asphalt. The bottoms are a black or dark brown material, which is very viscous or solid at ambient temperatures. The higher the flasher temperature, the more viscous the asphalt. There are two commonly used tests for grading this type of asphalt: softening point (Section 9.1.7) and penetration (Section 9.1.3).

A wide variety of grades of asphalt can be dispensed by a refinery by making blocked-out runs. The flasher unit can produce low penetration (e.g. 40-50) asphalt then adjusted to produce high penetration (e.g. 250) asphalt. Blending of these two grades yields asphalts of any grade between 40 and 250 penetration.

## 2.1 Asphalt Treatment and Properties

A number of procedures have been developed to achieve the desired properties needed for various asphalt applications. The procedures include oxygenation (blown asphalt), dilution (cutbacks) and emulsification (emulsions).

### 2.1.1 Blown Asphalt

Blowing hot air into an asphalt causes a chemical reaction whereby oxygen in the air bonds to hydrogen from the asphalt yielding water, which evaporates. A harder, more rubbery asphalt results. Lower penetration asphalts can be achieved via blowing, usually at a cost saving depending upon the composition of the asphalt.

### 2.1.2 Cutbacks

The application of asphaltic concrete requires that the material flows and that the asphalt binder completely surrounds the aggregate particles. Normally asphalt is mixed and applied at elevated temperatures to achieve these properties. To reduce the stringency of the equipment requirements necessitated by the elevated temperatures of the asphalt and at the same time achieve a hard durable product, a thinner is sometimes added to the asphalt. The

addition of a thinner will soften the asphalt and permit lower application temperatures. Upon application, the thinner evaporates, leaving a hard, durable asphalt. For a shorter curing time a very light thinner like naphtha can be used but for a longer curing time, kerosene can be used.

The thinners used simply pass through the system and do not remain in the finished product. They are, however, expensive and are a fire hazard. Thinners contribute, by evaporation, to air pollution and are possible sources of soil and groundwater contamination.

### 2.1.3 Emulsions

In order to achieve the same flexibility in field equipment as is achieved by using cutbacks while avoiding their detrimental aspects, emulsions have been developed. Emulsions are mixtures of 50-70% asphalt, 30-50% water and an emulsifying agent, comprising approximately 1%. Upon application, the water evaporates, as do the cutback thinners, leaving the hard asphalt behind but without the fire hazards and environmental problems inherent with cutbacks. Emulsions are usually applied at lower temperatures than any of the previously mentioned grades of asphalt.

Asphalt particles in emulsions are naturally negatively charged (anionic) as are the aggregates that are used with the asphalt. This renders the complete coating of the aggregate particles by the asphalt difficult to achieve. Emulsions have been developed in which the asphalt particles are positively charged (cationic) to promote the adhesion of the asphalt to the aggregate.

## 2.2 Composition and Durability

The question of the relationship between the chemical composition of asphalts and their durability in pavement mixtures was examined in detail by Petersen (1984). No laboratory work was undertaken, the work consisted entirely of a literature search, compilation, review, synthesis and interpretation of information. A copy of Petersen's paper can be viewed at the Minerals and Energy Division office, Fredericton, N.B.

### 2.2.1 Factors Affecting Asphalt Durability

The most important aspect of a durable asphalt, assuming it meets initial performance requirements, is its resistance to change during in-use service. The dominant physical property change leading to reduced asphalt durability is a change in flow properties related to excessive stiffening or hardening of the asphalt. Three fundamental composition-related factors govern the changes that could cause hardening of asphalts in pavements.

1. Loss of the oily components of asphalt by volatility or absorption by porous aggregates: this factor has been determined generally not to be significant.

2. Changes in the chemical composition of asphalt molecules from reaction with atmospheric oxygen: this factor has been determined to be the major and best understood factor.

3. Molecular structuring that produces thixotropic effects (stearic hardening):

this factor is thought to possibly be significant.

Irreversible adsorption of polar asphalt components by mineral aggregates will produce compositional changes in the asphalt that may also significantly affect asphalt properties and aging characteristics. Moisture induced damage may be related to asphalt composition and adsorption of asphalt components on aggregate surfaces.

### 2.2.2 Chemical Composition of Asphalt

Although asphalt is composed predominantly of carbon and hydrogen, most asphalts contain several heteroatoms which although minor, can vary widely in concentration. They often make a disproportionately large contribution to the differences in physical properties among asphalts from different sources. The heteroatoms, particularly nitrogen and oxygen and the aromatic carbon rings contribute considerable polarity or polarizability to the molecules which produce the intermolecular bonds that affect physical properties.

Three procedures are used to fractionate asphalt into less complex and more homogeneous fractions or components to permit its characterization and classification. They are:

1. Partitioning with partial solvents:
   The asphalt is sequentially treated with increasingly polar solvents (e.g. n-butanol and acetone) which precipitate a series of fractions with decreasing polarity.

2. Selective adsorption-desorption chromatography:
The asphaltenes are first separated based on their insolubility in a nonpolar paraffinic solvent (e.g. n-haptene) to remove the most polar and least soluble asphalt components and facilitate further separation. The remaining petrolene fraction, which is dissolved in the paraffinic solvent, is then adsorbed on a chromatographic column and sequentially desorbed with solvents of increasing polarity (e.g. n-haptene, benzene, methanol benzene and trichloroethylene). A series of fractions with increasing polarity are thereby obtained.

3. Chemical precipitation:
The asphaltenes are first separated utilizing n-pentane. The remaining components are sequentially separated into fractions based on their reactivity with sulphuric acid of increasing strength. An 85% sulphuric acid solution yields nitrogen compounds and many of the oxygenated molecules. Concentrated sulphuric acid is then used to precipitate an aromatic fraction, low in nitrogen. Sulphuric acid containing 30% $SO_3$, which is a strong sulphonating and complexing agent is used to precipitate those components with less reactive or polarizable aromatic ring systems. The remaining fraction consists of the paraffins.

### 2.2.3 Asphalt Aging

Asphalt reacts with atmospheric oxygen which stiffens or hardens the asphalt. As a result, pavement void content correlates strongly with asphalt pavement hardening. The change is, however, not due to loss of volatile components but is one of actual chemical oxidation of asphalt components. Generally, the change seen on oxidative aging is one of movement of components from nonpolar to the more polar fractions.

The relative amount of hardening is not solely related to the amount of oxidation. It also depends on the type of asphalt. For example, when comparing asphalts from different sources, they often show differing sensitivity to oxidation. They commonly have dissimilar compositions and thus their components interact differently upon oxidation. The variation in oxidation accounts for the resulting difference in viscosity.

The introduction of an antioxidant or other antidegradent has been found to be an effective method of increasing the durability of asphaltic concretes. Of specific interest to New Brunswick but not necessarily relative to shale oil asphalt development is research which was undertaken by Matrecon Inc. of Oakland California and sponsored by the International Lead-Zinc Research Organization Inc. (Radkte and Carr, 1983). Diaikyldithiocarbamates, a family of antioxidants/antidegradants have been used for several years to combat the effects of aging on such products as rubbers, plastics, paints, lubricating oils and food. It was found that lead diamyldithiocarbamate (LDADC) when added to asphalt in concentrations of one to two parts per hundred of asphalt retarded asphalt hardening

in both laboratory and field tests. Interest in these test results has been expressed by Brunswick Mining and Smelting who is actively pursuing this avenue as a new market for lead.

### 2.2.4 Chemical Factors Affecting Asphalt Durability

The physical properties of asphalt are controlled by the interactions of the molecules from which it is composed, therefore an understanding of these interactions should provide the basis for understanding its physical behaviour and thus its durability. Many molecules of different composition have similar features of "functionality" that will produce similar effects on physical properties. Functionality analysis has the advantage over component fractionation in that it can take into account the multiple functionality of asphalt molecules.

Nonpolar hydrocarbon components in asphalt such as those dominant in the saturate fraction exhibit weak interaction forces thus accounting for the fluid character of this fraction. Asphalt components containing highly condensed ring systems and chemical functional groups containing oxygen and nitrogen atoms may be highly polar or polarizable and thus interact strongly with each other. These strong interaction forces largely account for the fact that asphaltenes, even though they may not be significantly different in molecular weight than the saturates melt at considerably higher temperature.

Oxygen, nitrogen and some forms of sulphur may introduce high polarity into molecules and although only a minor component, can exhibit a controlling influence on the molecular interactions that control asphalt viscosity

properties. Nitrogen, which occurs in concentrations of 0.2 - 1%, is present in several forms from the slightly acidic pyrrole types to the more basic and strongly interacting pyridine types.

If, during aging, the concentration of polar functional groups becomes sufficiently high to cause molecular immobilization through increased intermolecular interaction forces, fracturing will result from the increase in brittleness of the asphalt. The treatment of asphalt with hydrated lime results in the removal of carboxylic acids and other highly polar functional groups that would have otherwise interacted with oxidation products to increase asphalt viscosity. The flow properties and hardening rate of asphalt might also be significantly altered by manipulation of molecular interactions through chemical modification or the addition of modifiers that can interact with polar chemical functionality in the asphalt and alter its activity. Antistripping agents, such as amines, alter asphalt viscosity. They interfere with molecular structure buildup and subsequent viscosity increase in asphalts. Cationic asphalt additives augment the peptization of the asphaltene constituent in many asphalts and thus reduce asphalt hardening rate.

Compatibility in asphalt deals with the mutual solubility of a variety of components with widely differing solubility and solvent powers. Asphalt compatibility can be changed for better or for worse by blending. The initial properties of each participating asphalt are not necessarily additive in determining final blend properties.

Molecular structuring or "stearic hardening" is a reversible phenomenon that can produce large changes in the

flow properties of asphalt without altering the chemical composition of the asphalt molecules. At ambient temperatures, structuring is a slow process which may go on for days or even years. Test evidence shows it is accelerated on mineral aggregate surfaces.

It appears that oxidation which takes place during the natural aging of asphalts in pavements significantly increases the rate of structural hardening and that oxidative and structural hardening may be synergistic. Structuring is destroyed during the solvent recovery of asphalts from aged pavements and therefore escapes detection during measurement of recovered asphalt properties. Thus, the tendency for an asphalt to harden from structuring, which may be a major contributor to loss of durability and pavement failure, is being virtually ignored in pavement performance consideration.

### 2.2.5 Summary

Asphalt chemical composition can vary widely with asphalt source and a variety of combinations of asphalt components with varying chemical structures in individual asphalts may produce asphalts that will provide satisfactory service. It therefore seems unlikely that satisfactory chemical composition specifications can be devised for asphalts. Such specifications would likely exclude from use many asphalts that would otherwise perform satisfactorily. Ideally, specifications should define the performance properties desired. Chemical information would be important in producing asphalts that meet the performance criteria.

Composition information is useful in understanding asphalt behaviour. With given asphalt sources available,

composition information can be used to improve the product through modification with additives or by blending, or to alter design specifications to accommodate specific properties. Composition information can be used to match asphalt and aggregate, provide clues regarding modifications necessary to make an asphalt-aggregate system more serviceable under a given environment, diagnose failures and provide information needed in taking corrective measures.

## 3.0 LITERATURE SUMMARY: SHALE OIL ASPHALTS

Studies were undertaken at Texas A & M University, sponsored by the Laramie Energy Technology Center (now the Western Research Institute of the University of Wyoming Research Corporation), in the late 1970's for the purpose of determining the suitability of shale-oil asphalt for use as pavement binder. It was found that the shale oil asphalts exhibited lower water susceptibility than petroleum asphalts. One of the major causes of asphalt pavement failure is moisture-induced damage, either the direct effects of moisture and/or through repeated freeze-thaw cycles. The suggestion that asphalt prepared from shale oil is less susceptible to water penetration than those of petroleum-derived asphalts resulted in a concerted effort to determine the exact nature of and reasons for these enhanced properties of durability.

It was found that pyridine-type nitrogen reduced the effects of moisture damage in asphaltic pavements. Nitrogen of the pyridine type is naturally present in asphalts in varying amounts but shale oil from the Green River Formation (Colorado, Utah, Wyoming) contains significant amounts (1.3 wt.%) of pyridine-type homologs. The strength of the nitrogen compound-aggregate bond was investigated. As a result, it was determined that the relative strength or stability of the nitrogen-aggregate bond yields the superior water susceptibility characteristics of the shale oil asphaltic concretes.

Studies also determined that nitrogen-rich shale oil fractions have the ability to disperse asphaltenes in oxidatively-aged petroleum asphalts. Pavement recycling requires the use of agents to restore desired viscoelastic

properties to the embrittled asphalt binder. It appears that nitrogen-rich shale oil derivatives could in fact be used as such agents, often with results better than those seen in use in current commercial products. Interestingly and contrary to these findings, pure shale oil asphalts have been found to be reactive with atmospheric oxygen. Asphalt oxidation leads to age hardening or embrittlement which results in premature pavement cracking and reduced pavement life. Preliminary studies have indicated that mixtures of shale oil and petroleum asphalts overcome the accelerated oxidation to which shale oil asphalts appear prone while maintaining the low water susceptibility characteristics of shale oil asphalts.

Six key research papers effectively detail the work which has been undertaken to date on the subject of shale oil asphalt durability. Copies of these papers, (Peterson 1984; Button et al. 1980; Plancher et al. 1980; Plancher et al. 1982; Plancher and Petersen 1984; and Petersen 1986), are available for viewing at the Minerals and Energy Division office, Fredericton, N.B. The research completed to date has progressed in an orderly, stepwise manner with each investigation leading into the next. Summaries of these papers follow in chronological order of their publication.

A number of the terms used and test procedures referred to in the research undertaken are specific to the pertroleum refining and asphalt industries. In order to facilitate comprehension of the text, a summary of Standard Test Procedures has been prepared and is included as an Appendix, Section 9.1.

## 3.1 Initial Laboratory Evaluation of Shale Oil Asphalts

Button et al. (1980) undertook laboratory evaluations of shale oil asphalts to determine their suitability for paving purposes. Selected shale-oil asphalt cements were characterized both by tests commonly used to specify paving asphalt and by certain special tests. Asphalt-aggregate mixtures were made by using the selected shale-oil asphalts and they too were subjected to tests that are used in specifying paving mixtures. The test results were then compared with similar characteristics of petroleum asphalt cements and petroleum asphalt-aggregate mixtures.

### 3.1.1 Asphalt Cement Properties

Crude shale oil was produced from oil shale from the Green River Formation in Colorado by a gas combustion process. Three viscosity-graded asphalt cements were produced:

1. AC-5: a soft asphalt cement produced by vacuum distillation.

2. AC-10: a solvent-extracted asphalt cement produced by a high-pressure process using an aliphatic solvent (by Kerr-McGee Co.).

3. AC-20: a hard asphalt cement produced by vacuum distillation.

The control asphalt was a viscosity-graded AC-10 petroleum asphalt cement produced by vacuum reduction by the American Petrofina Co.

American Society for Testing and Materials (ASTM), American Association of State Highway and Transportation Officials (AASHTO) and other standard laboratory tests were performed on each asphalt to determine physical and chemical characteristics, including consistency, durability, purity and safety (Table 3.1.1; Section 9.1).

### 3.1.2 Aggregate Properties

Two types of aggregates were selected for use in the research.

1. A gravel composed of subrounded siliceous clasts.

2. A crushed very hard limestone.

Standard tests were conducted to determine bulk specific gravity, saturated surface dry (SSD) bulk specific gravity, apparent specific gravity, absorption capacity, abrasion resistance and unit weight (Table 3.1.2). An additional test was conducted to estimate the optimum asphalt content.

**TABLE 3.1.1 ORIGINAL ASPHALT CEMENT PROPERTIES**

| Characteristic Measured | Laboratory Standard AC-10 | AC-5 | AC-10 | AC-20 |
|---|---|---|---|---|
| Viscosity (Pa-s) (Sections 9.1.10 & 9.1.11) | | | | |
| 25°C (x $10^4$) | 5.8 | 4.8 | 26 | 25 |
| 60°C | 158 | 49 | 130 | 199 |
| 135°C | 0.38 | 0.13 | 0.23 | 0.22 |
| Penetration (mm) (Section 9.1.3) | | | | |
| 25°C | 11.8 | 12.3 | 4.3 | 7.0 |
| 4°C | 2.6 | 3.2 | 0.8 | 3.1 |
| Softening point, ring and ball (°C) (Section 9.1.7) | 42 | 46 | 48 | 49 |
| Penetration index (Section 9.1.3) | -1.4 | +0.25 | -1.9 | -0.5 |
| Specific gravity at 25°C | 1.02 | 1.01 | 1.03 | 1.03 |
| Ductility at 25°C (cm) | 150+ | 127 | 150+ | 93 |
| Solubility (CH Cl:$CCl_2$) (%) | 99.99 | 100 | 99.97 | 100 |
| Flash point (°C) (Section 9.1.1) | 324 | 306 | 294 | 271 |
| Fire point (°C) (Section 9.1.1) | 370 | 355 | 334 | 308 |
| Spot test (Section 9.1.8) | Negative | Negative | Negative | Negative |
| Thin-film oven test (Section 9.1.9) | | | | |
| Penetration of residue at 25°C | 68 | 48 | 24 | 22 |
| Ductility of residue at 25°C | 150+ | 148 | 150+ | 9 |
| Viscosity of residue at 60°C | 3050 | 2070 | 3650 | Too high |
| Loss of heating (%) | Negative | Negative | Negative | 2 |
| Hardening index (actinic light) | 1.9 | 2.5 | 2.2 | 1.7 |
| Vanadium content (ppm) | 3.4 | 2.6 | -- | 3.2 |

Note: 1 Pa-s = 10 poises; t°C = (t°F - 32)1.8; 1 mm = 0.04 in.

**TABLE 3.1.2 PHYSICAL PROPERTIES OF AGGREGATES**

| Aggregate Grading | Test Designation | Physical Property | Test Results: Gravel | Test Results: Limestone |
|---|---|---|---|---|
| Coarse material[a] | ASTM C127, AASHTO T85 | Bulk specific gravity | 2.261 | 2.663 |
| | | SSD bulk specific gravity | 2.640 | 2.678 |
| | | Apparent specific gravity | 2.672 | 2.700 |
| | | Absorption (%) | 0.72 | 0.7 |
| Fine material[b] | ASTM C218, AASHTO T84 | Bulk specific gravity | 2.551 | 2.537 |
| | | SSD bulk specific gravity | 2.597 | 2.597 |
| | | Apparent specific gravity | 2.675 | 2.702 |
| | | Absorption (%) | 1.8 | 2.2 |
| | Centrifuge kerosene equivalent | Surface capacity (% by weight of dry aggregate | 3.0 | 4.1 |
| Project design gradation | ASTM C127 and C128, AASHTO T84 and T85 | Bulk specific gravity | 2.580 | 2.589 |
| | | Apparent specific gravity | 2.671 | 2.701 |
| | | Absorption (%) | 1.3 | 1.56 |
| | ASTM C29, AASHTO T19 | Compacted unit weight ($kg/m^3$) | 2066 | 1954 |
| | Centrifuge kerosene equivalent and oil equivalent | Estimated optimum asphalt content (% by weight of dry aggregate) | 4.7 | 5.5 |
| Grading C | ASTM C131, AASHTO T96 | Abrasion resistance (% loss) | 19 | 23 |
| <9.5 mm to >4.75 mm | Oil equivalent | Surface capacity (% oil retained by weight of dry aggregate) | 1.8 | 2.3 |

Note: 1 $kg/m^3$ = 0.06 lb/ft

[a]Material retained on 4.75-mm (no. 4) sieve from project design gradation.

[b]Material passing 4.75-mm (no. 4) sieve from project design gradation.

### 3.1.3 Performance of Shale-Oil Asphalts in Paving Mixtures

A series of tests were undertaken on actual paving mixtures manufactured from the four asphalts (one standard and three shale oil) utilizing the two aggregates. Both gyratory and Marshall compacted specimens were prepared and tested (Section 9.1).

The physical properties of the various paving mixtures prepared by gyratory compaction are presented in Table 3.1.3. These measured properties provide a comparison between the laboratory standard asphalt and the three shale oil asphalts utilizing the two different aggregates.

**TABLE 3.1.3 BASIC PHYSICAL PROPERTIES OF GYRATORY-COMPACTED SPECIMENS**

| Physical Property | Laboratory Standard | Rounded Gravel Aggregate AC-5 | AC-10 | AC-20 |
|---|---|---|---|---|
| Bulk specific gravity of compacted mix | 2.43 | 2.40 | 2.42 | 2.42 |
| Maximum specific gravity of mixture | 2.50 | 2.51 | 2.50 | 2.50 |
| Asphalt absorption (% by weight of aggregate) | 1.0 | 1.2 | 0.91 | 0.91 |
| Effective asphalt content (% of total mix) | 2.7 | 2.5 | 2.8 | 2.8 |
| Voids in mineral aggregate (VMA) (% of bulk volume) | 9.3 | 10.4 | 9.6 | 9.6 |
| Air void content (% of total volume) | 2.8 | 4.4 | 3.2 | 3.2 |
| VMA filled with asphalt (% of VMA) | 76 | 67 | 73 | 73 |

| Physical Property | Laboratory Standard | Crushed Limestone Aggregate AC-5 | AC-10 | AC-20 |
|---|---|---|---|---|
| Bulk specific gravity of compacted mix | 2.42 | 2.45 | 2.45 | 2.46 |
| Maximum specific gravity of mixture | 2.51 | 2.50 | 2.52 | 2.51 |
| Asphalt absorption (% by weight of aggregate) | 1.6 | 1.3 | 1.6 | 1.3 |
| Effective asphalt content (% of total mix) | 2.8 | 3.1 | 2.8 | 3.0 |
| Voids in mineral aggregate (VMA) (% of bulk volume) | 10.6 | 9.5 | 9.5 | 9.1 |
| Air void content (% of total volume) | 3.6 | 2.0 | 2.8 | 2.0 |
| VMA filled with asphalt (% of VMA) | 74 | 84 | 79 | 84 |

Note: Each value represents an average of 30 specimens

The resilient modulus (Table 3.1.4; Section 9.1.2) indicates that the order of stiffness of the asphalt mixtures is the same regardless of aggregate. The order of stiffness from low to high is: lab. standard, AC-5, AC-20 and AC-10. The coefficients of variation (up to 17) are considered reasonable; coefficients of 10% or less are considered excellent.

**TABLE 3.1.4 STATISTICS OF RESILIENT MODULUS OF GYRATORY-COMPACTED SPECIMENS AT 20°C**

| | Rounded Gravel Aggregate | | | |
|---|---|---|---|---|
| Physical Property | Laboratory Standard | AC-5 | AC-10 | AC-20 |
| Mean resilient modulus (kPa x $10^6$) | 3.55 | 6.55 | 13.0 | 8.47 |
| SD (kPa x $10^6$) | 0.414 | 1.13 | 1.07 | 1.31 |
| Coefficient of variation (%) | 12 | 17 | 8 | 16 |

1kPa - 0.145 psi

| | Crushed Limestone Aggregate | | | |
|---|---|---|---|---|
| Physical Property | Laboratory Standard | AC-5 | AC-10 | AC-20 |
| Mean resilient modulus (kPa x $10^6$) | 4.98 | 7.35 | 13.4 | 9.79 |
| SD (kPa x $10^6$) | 0.69 | 0.73 | 1.47 | 1.04 |
| Coefficient of variation (%) | 14 | 10 | 11 | 11 |

1kPa - 0.145 psi

The results of the splitting tensile test (Table 3.1.5; Section 9.1.2) are expected to yield the highest tensile strength and highest elastic modula at the highest loading rate and the lowest temperature (the converse for tensile strain). This trend is fairly consistent although there are instances contrary to this trend. The lack of precision in the data, in homogeneity of the speciments and the testing of only three specimens per asphalt/aggregate mix contribute to the inconsistency seen.

**TABLE 3.1.5 SUMMARY OF SPLITTING TENSILE TEST DATA**

| Displacement Rate (cm/min) | Temperature (°C) | Laboratory Standard Stress (Pa) | Laboratory Standard Strain (cm/cm) | Laboratory Standard Modulus (kPa) | AC-5 Stress (Pa) | AC-5 Strain (cm/cm) | AC-5 Modulus (kPa) | AC-10 Stress (Pa) | AC-10 Strain (cm/cm) | AC-10 Modulus (kPa) | AC-20 Stress (Pa) | AC-20 Strain (cm/cm) | AC-20 Modulus (kPa) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Gravel** | | | | | | | | | | | | | |
| 5.1 | 20 | 110 | 0.0029 | 38 | 140 | 0.0026 | 58 | 310 | 0.0038 | 82 | 160 | 0.0025 | 75 |
| | 1 | 390 | 0.0027 | 170 | 410 | 0.0013 | 354 | 450 | 0.0007 | 984 | 400 | 0.0009 | 470 |
| | -25 | 490 | 0.0012 | 418 | 380 | 0.0006 | 625 | 340 | 0.0004 | 1042 | 370 | 0.0006 | 668 |
| Soak | 20 | 100 | 0.0050 | 21 | 200 | 0.0026 | 76 | 200 | 0.0038 | 55 | 230 | 0.0020 | 114 |
| 0.51 | 20 | 50 | 0.0043 | 12 | 80 | 0.0032 | 25 | 230 | 0.0032 | 87 | 100 | 0.0023 | 46 |
| | 1 | 250 | 0.0020 | 130 | 380 | 0.0018 | 212 | 400 | 0.0016 | 257 | 300 | 0.0014 | 232 |
| | -25 | 380 | 0.0009 | 498 | 460 | 0.0008 | 578 | 370 | 0.0009 | 457 | 430 | 0.0009 | 519 |
| 0.051 | 20 | 20 | 0.0041 | 5 | 30 | 0.0037 | 9 | 80 | 0.0048 | 18 | 60 | 0.0022 | 30 |
| | 1 | 110 | 0.0018 | 59 | 110 | 0.0021 | 61 | 250[a] | 0.0024[a] | 102[a] | 340 | 0.0011 | 348 |
| | -25 | 340 | 0.0012[a] | 331[a] | 270 | 0.0011 | 246 | 390[b] | 0.0014[b] | 271[b] | 410 | 0.0011 | 385 |
| **Limestone** | | | | | | | | | | | | | |
| 5.1 | 20 | 150 | 0.0025 | 60 | 130 | 0.0023 | 69 | 250 | 0.0029 | 89 | 150 | 0.0017 | 94 |
| | 1 | 520 | 0.0018 | 298 | 480[a] | 0.0011[a] | 462[a] | 590 | 0.0006 | 1089 | 500 | 0.0011 | 479 |
| | -25 | 630[a] | 0.0012[a] | 533[a] | 500 | 0.0011 | 553 | 470 | 0.0005 | 955 | 590 | 0.0010 | 598 |
| Soak | 20 | 90 | 0.0059 | 16 | 120 | 0.0038 | 32 | 190 | 0.0031 | 63 | 240 | 0.0022 | 109 |
| 0.51 | 20 | 90 | 0.0041 | 23 | 70 | 0.0034 | 19 | 270 | 0.0030 | 97 | 120 | 0.0017[a] | 70[a] |
| | 1 | 310 | 0.0022 | 150 | 420 | 0.0013 | 337 | 490 | 0.0014 | 361 | 400 | 0.0014 | 280 |
| | -25 | 630 | 0.0030[a] | 226[a] | 540 | 0.0012 | 479 | 470 | 0.0011 | 456 | 600 | 0.0012 | 500 |
| 0.051 | 20 | 40 | 0.0040 | 11 | 40 | 0.0028 | 12 | 90 | 0.0042 | 21 | 70 | 0.0023 | 32 |
| | 1 | 140 | 0.0021 | 70 | 470 | 0.0014 | 340 | 380[a] | 0.0020[a] | 200[a] | 200 | 0.0017 | 120 |
| | -25 | 410 | 0.0030 | 156 | 500 | 0.0011 | 481 | 480[a] | 0.0024[a] | 205[a] | 570 | 0.0013 | 462 |

Notes: 1 cm = 0.4 in; t°C = (t°F -32)/1.8; 1 kPa = 0.145 psi.
All values measured at the point of failure.

[a]Average of two specimen values. [b]Single specimen value.

The manufactured asphalt mixtures were subsequently "broken down" and the asphalts recovered and analyzed. Comparison of the properties of the recovered asphalts (Table 3.1.6) with those of the original asphalts (Table 3.1.1) indicates that as a result of heating during mixing and compacting:

1. Penetration at 25°C for all asphalts decreased approximately 50%.
2. Viscosity at 25°C for all asphalts increased by approximately one order of magnitude.
3. Viscosity at 60°C for soft asphalts (lab std. and AC-5) increased by 3.
4. Viscosity at 60°C for hard asphalts (AC-10 and AC-20) increased by 7 and 16, respectively.
5. Some hardening of the shale oil asphalts was noted.

**TABLE 3.1.6 RECOVERED ASPHALT PROPERTIES**

| Aggregate | Test | Laboratory Standard | AC-5 | AC-10 | AC-20 |
|---|---|---|---|---|---|
| Extracted from gravel | Penetration at 25°C (mm) | 5.5 | 4.6 | 1.9 | 3.0 |
| | Viscosity (Pa-s) | | | | |
| | 25°C (x $10^5$) | 3.9 | 2.8 | 23 | 20 |
| | 60°C | 463 | 143 | 881 | 3300 |
| | Ring and ball softening point (°C) | 54 | 57 | 57 | 67 |
| Extracted from limestone | Penetration at 25°C (mm) | 5.3 | 5.0 | 1.7 | 3.5 |
| | Viscosity (Pa-s) | | | | |
| | 25°C (x $10^5$) | 3.8 | 3.2 | 24 | 15 |
| | 60°C | 432 | 152 | 801 | 1310 |
| | Ring and ball softening point (°C) | 54 | 49 | 58 | 61 |

Note: $t°C = (t° F - 32)/1.8$; 1 Pa-s = 10 poises.

A medium traffic category asphalt mix requires a Marshall stability (Section 9.1.3) greater than 2224 N; all mixtures exceeded this value. All three shale oil mixes using rounded gravel aggregate exceeded the laboratory standard asphalt mix. Only the AC-20 mix, using crushed limestone aggregate exceeded the laboratory standard asphalt mix.

**TABLE 3.1.7 BASIC PHYSICAL PROPERTIES OF MARSHALL-COMPACTED SPECIMENS**

| Physical Property | Rounded Gravel Aggregate | | | |
|---|---|---|---|---|
| | Laboratory Standard | AC-5 | AC-10 | AC-20 |
| Bulk specific gravity of compacted mix | 2.44 | 2.42 | 2.43 | 2.39 |
| Maximum specific gravity of mixture | 2.49 | 2.51 | 2.50 | 2.50 |
| Asphalt absorption (% by weight of aggregate) | 0.75 | 1.2 | 0.91 | 0.91 |
| Effective asphalt content (% of total mix) | 2.9 | 2.5 | 2.8 | 2.8 |
| Voids in mineral aggregate (VMA) (% of bulk volume) | 9.1 | 9.8 | 9.3 | 10.8 |
| Air void content (% of total volume) | 2.1 | 3.7 | 2.8 | 4.2 |
| VMA filled with asphalt (% of VMA) | 80 | 70 | 76 | 67 |
| Marshall stability (N) | 5650 | 6140 | 6850 | 10,990 |
| Marshall flow (mm) | 1.8 | 1.5 | 1.5 | 1.8 |
| Resilient modulus at 20°C (kPa) | 3930 | 7860 | --- | 11,170 |

| Physical Property | Crushed Limestone Aggregate | | | |
|---|---|---|---|---|
| | Laboratory Standard | AC-5 | AC-10 | AC-20 |
| Bulk specific gravity of compacted mix | 2.45 | 2.42 | 2.46 | 2.42 |
| Maximum specific gravity of mixture | 2.53 | 2.50 | 2.52 | 2.51 |
| Asphalt absorption (% by weight of aggregate) | 1.7 | 1.3 | 1.6 | 1.3 |
| Effective asphalt content (% of total mix) | 2.6 | 3.1 | 2.7 | 3.0 |
| Voids in mineral aggregate (VMA) (% of bulk volume) | 10.5 | 10.7 | 9.1 | 10.6 |
| Air void content (% of total volume) | 3.0 | 3.5 | 2.3 | 3.6 |
| VMA filled with asphalt (% of VMA) | 78 | 75 | 81 | 74 |
| Marshall stability (N) | 12,190 | 10,270 | 11,390 | 15,260 |
| Marshall flow (mm) | 2.8 | 2 | 3 | 2.5 |
| Resilient modulus at 20°C (kPa) | 4070 | 8000 | --- | 11,580 |

Note: 1N = 0.225 lbf; 1 mm = 0.4 in; $t^{\circ}C = (t^{\circ}F - 32)/1.8$; 1 kPa = 0.145 psi

The susceptibility of the asphalt mixtures to water "damage" was determined by measuring the resilient modula and splitting tensile strength of samples saturated with water. The resilient modula of the asphalt mixtures prepared with the laboratory standard asphalt and AC-10 with both aggregates were adversely affected by soaking in water, whereas the mixtures that used AC-5 and AC-20 were not appreciably affected (Table 3.1.8). Similar results were generally found in the postsoaking results of the splitting tensile tests. Asphalts AC-5 and AC-20 are both shale oil based and produced by vacuum distillation. The laboratory standard asphalt is petroleum based and AC-10 was produced by solvent extraction, not distillation.

**TABLE 3.1.8 WATER SUSCEPTIBILITY TESTS**

| Physical Property | Laboratory Standard | Rounded Gravel Aggregate* AC-5 | AC-10 | AC-20 |
|---|---|---|---|---|
| Resilient modulus at 20°C (kPa) | | | | |
| before soaking | 3 | 7 | 12.4 | 9.3 |
| after soaking | 2 | 7.1 | 7.5 | 10.8 |
| Splitting tensile strength (kPa) | | | | |
| before soaking | 680 | 850 | 2000 | 1000 |
| after soaking | 600 | 1250 | 1250 | 1500 |

* Results for crushed limestone aggregate were not available.

### 3.1.4 Conclusions

As a result of the various tests conducted, it was concluded that Green River Formation shale oil asphalt can be produced by conventional methods in acceptable grades for

highway paving mixtures. The adhesive properties of the shale-oil asphalt tested were found to be sufficient to produce adequate paving mixtures and compare favorably with those of petroleum asphalts. Most importantly, it was concluded that paving mixtures that contain Green River Formation shale-oil asphalts appear to show superior resistance to damage by water but that mixtures prepared from the solvent-precipitated asphalt showed some water susceptibility and possibly some loss of Marshall stability.

Hardening of the Green River Formation shale-oil asphalts as a result of heating during mixing and compacting was found to be slightly higher than that of the petroleum asphalt. This indication of susceptibility to oxidative hardening, a feature detrimental to pavement durability, is addressed specifically in Section 3.4.

## 3.2 Investigation of Performance of Shale Oil Asphalts

Plancher et al. (1980) supplemented and extended earlier studies by providing explanations for some of the unusual performance properties imparted to bituminous concrete mixtures by using products derived from shale oil. The bonding characteristics of a shale oil asphalt coated aggregate surface were studied by analyzing the chemical components adsorbed on the mineral aggregate surface and their subsequent displacement from the surface by water and pyridine. These test results from the bonding studies were confirmed using a model experiment and by analyzing samples taken from a 27-year-old pavement constructed from shale oil residues.

### 3.2.1 Materials

Materials used to undertake the various tests included aggregate, a sample of an actual shale-oil-derived pavement, shale oil and petroleum asphalts, a shale oil nitrogen concentrate and various solvents. The aggregates used originated from two sources, a limestone from Washington, D.C. and a quartzite from Wolcott Junstien, Wyoming. The sample of shale oil pavement was taken from the Anvil Points road near Rifle, Colorado which was constructed in the early 1950's using locally produced shale oil residue as a binder. The shale oil asphalt was an AC-5 viscosity-graded asphalt prepared by vacuum distillation of a shale oil residue from Green River Formation oil shale. The oil shale was produced by a gas combustion process.

### 3.2.2 Procedures and Results

Aggregates were heat coated with shale oil asphalts. The aggregates were then stripped of asphalt in a three-step process. Asphalt-coated aggregates were first stripped of nonadsorbed asphalt (NA) using benzene. The NA aggregates were then stripped of strongly adsorbed asphalt by using water (SA/WD), vacuum and freeze-thaw cycles. The SA/WD aggregates were subsequently stripped of strongly adsorbed asphalt not previously displaceable by water (SA/NWD) by using pyridine. The compositions of the original shale oil asphalt and the four stripped fractions were determined (Table 3.2.1). Ketones, carboxylic acids, dicarboxylic anhydrides, sulphoxide concentrations and 2-quinolone types were quantified by a differential infrared spectrometric technique. Phenolic-OH and pyrrolic-NH concentrations were measured by selective chemical reaction and differential infrared spectroscopy. Nitrogen contents were determined on a chemiluminescent nitrogen analyzer.

**TABLE 3.2.1 CHEMICAL COMPOSITION OF VARIOUSLY ADSORBED OIL SHALE ASPHALT COMPONENTS**

| Asphalt or Fraction | Wt % of Total Asphalt | Total N, Wt % | Concentration, mol/liter | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Pyrrolic NH | Phenolic OH | Ketones | Carboxylic Acids | Dicarboxylic Anhydrides | Sulfoxides | 2-Quinolones |
| Original shale-oil asphalt | 100.00 | 4.01 | 0.5 | --- | 0.44 | trace | 0.015 | 0.025 | 0.045 |
| NA fraction | 99.75 | 4.01 | 0.5 | 0.75 | 1.1 | 0.026 | 0.07 | 0.025 | 0.045 |
| SA/WD fraction | 0.014 | 3.91 | N.D | N.D. | trace | 0.08 | 0.38 | N.D. | 0.62 |
| SA/NWD fraction | 0.234 | 4.37 | 0.10 | 1.0 | 0.78 | 0.22 | 0.20 | N.D. | 0.12 |
| SA[1] fraction | 0.248 | 4.35 | 0.094 | 0.94 | 0.74 | 0.212 | 0.210 | -- | 0.148 |

[1] Total strongly adsorbed (calculated values from SA/WD and SA/NWD)
ND: not detectable

A high ratio of total nitrogen to carboxylic acids is involved in the bonding process as evidenced by the analyses of the stripped shale oil asphalt (Table 3.2.1). This appears to be a major factor contributing to superior moisture damage resistance of shale oil-asphalt mixtures.

Aggregates were pretreated with pyridine prior to utilization in asphalt mixtures. Manufactured asphalt-aggregate briquets were subjected to freeze-thaw cycles to the point of failure in order to determine their resistance to moisture damage. Comparison between the number of freeze-thaw cycles required to failure in petroleum versus shale oil asphalt briquets (Table 3.2.2) show that the shale oil briquet is more resistant to moisture damage.

**TABLE 3.2.2 EVALUATION OF MANUFACTURED BRIQUETS**

| | Briquet Weight, g | Cycles to Failure |
|---|---|---|
| Petroleum Asphalts: | | |
| B-2959 | 50 | 1 |
| B-3036 | 50 | 2 |
| B-3051 | 50 | 7 |
| B-3602 | 50 | 2 |
| Shale Oil Asphalt: | | |
| Shale Oil | 50 | > 18 (>100)* |

* Later reported to be >100 (Plancher and Peterson, 1984; to follow).

The nitrogen content of the shale oil asphalt (Table 3.2.1) is 3.65 to 15.42 times greater than the nitrogen content of the four petroleum-based asphalts (Table 3.2.3) used to manufacture the test briquets (Table 3.2.2).

**TABLE 3.2.3 ELEMENTAL ANALYSES OF PETROLEUM ASPHALTS (PETERSON, 1984)**

| Code / Source | | B-2959 Mexican Blend | B-3038 Arkansas-Louisiana | B-3051 Boscan | B-3602 California |
|---|---|---|---|---|---|
| Carbon | (%) | 83.77 | 85.78 | 82.90 | 86.77 |
| Hydrogen | (%) | 9.91 | 10.19 | 10.45 | 10.94 |
| Nitrogen | (%) | 0.28 | 0.26 | 0.78 | 1.10 |
| Sulphur | (%) | 5.25 | 3.41 | 5.43 | 0.99 |
| Oxygen | (%) | 0.77 | 0.36 | 0.29 | 0.20 |
| Vanadium | (ppm) | 180 | 7 | 1380 | 4 |
| Nickel | (ppm) | 22 | 0.4 | 109 | 6 |

Trace amounts of a shale oil nitrogen concentrate were added to a petroleum asphalt-aggregate mixture prior to manufacturing test briquets. The briquets were then subjected to freeze-thaw cycles to the point of failure in order to determine the effect of the shale oil additive to their resistance to moisture damage. The test results cited on Table 3.2.4 indicate that the shale oil additive significantly increases resistance to moisture damage.

**TABLE 3.2.4 EVALUATION OF ADDING SHALE OIL NITROGEN (CONCENTRATE) TO MANUFACTURED BRIQUETS**

| Wt., g | | | |
|---|---|---|---|
| Asphalt B-3051 | Additive Shale Oil | Aggregate Quartzite | Cycles To Failure |
| 5.00 | 0 (Control) | 95 | 1 |
| 4.95 | 0.05 | 95 | 2 |
| 4.75 | 0.25 | 95 | 5 |
| 4.50 | 0.50 | 95 | 6 |

The shale-oil-derived asphalt binder from a still serviceable 27 year old pavement sample from Anvil Points, Colorado was selectively desorbed and analyzed. The pavement sample prior to extraction showed no visual evidence of water stripping of the binder. Nonadsorbed (NA), strongly adsorbed/water displaced (SA/WD) and strongly adsorbed/not displaceable by water (SA/NWD) fractions were extracted and analyzed (Table 3.2.5). The significant result is that the SA/NWD fraction is higher in nitrogen than the NA fraction, which is consistent with previous observations that basic nitrogen compounds are strongly adsorbed on aggregate surfaces.

**TABLE 3.2.5 CHEMICAL ANALYSIS OF ANVIL POINTS SHALE OIL PAVEMENT EXTRACTS**

| | | | Concentration, mol/liter | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Carboxylic Acids | | | | |
| Binder, Fraction | Wt % of Total pavement | Total N, wt % | Pyrrolic NH | Phenolic OH | Ketones | Free | Salts | Total | Dicarboxlic anhydrides | 2-Quinolones |
| NA | 4.35 | 2.70 | 0.6 | 0.15 | 1.4 | 0.045 | 0.029 | 0.074 | 0.124 | 0.036 |
| SA/WD | 0.13 | 5.84 | 0.4 | 0.46 | 1.3 | 0.16 | 0.03 | 0.19 | 0.276 | 0.14 |
| SA/NWD | 0.49 | 3.40 | 0.7 | 0.39 | 1.7 | 0.044 | 0.087 | 0.13 | 0.18 | 0.085 |

### 3.2.3 Conclusions

Evidence shows that nitrogen compounds may be responsible for increased resistance of bituminous concrete mixtures to moisture damage.

Basic nitrogen compounds can compete successfully with the carboxylic acids for aggregate surface bonding sites.

Shale-oil-derived asphalts or the addition of basic nitrogen compounds to petroleum asphalt-aggregate mixtures significantly reduce the susceptibility of the pavement mixtures to moisture damage.

Nitrogen-bearing compounds are considered deleterious in shale oil utilized for fuel. On the other hand, nitrogen compounds may have promising potential in pavement applications.

## 3.3 Nitrogen Compounds as Asphalt Modifiers

Plancher et al. (1982) and Plancher and Petersen (1984) evaluated shale-oil- and coal-derived materials for use as moisture damage inhibitors and/or recycle agents in asphalt paving applications. They utilized programmed time-temperature desorption of nitrogen compounds from aggregates followed by chemiluminescent measurement of the nitrogen evolved.

### 3.3.1 Materials

Materials used to undertake the various tests included aggregates, asphalts and asphalt additives. The aggregates were obtained from established paving sources. The asphalts used consisted of AC-5 and AC-10 viscosity-graded asphalts both naturally and artificially aged. The additives consisted of:

1. A shale oil nitrogen concentrate.
2. A petrolene fraction from a shale oil asphalt.
3. A shale oil distillate.
4. Two distillate fractions from coal liquids.
5. Several commercially available recycle agents.

### 3.3.2 Procedures

Aggregates were treated with nitrogen-bearing benzene solutions. Half of the treated aggregates were further

treated by a water/benzene solution to remove water-displaceable nitrogen compounds from the aggregate surface.

Elemental nitrogen analyses were obtained on 0.25g of treated aggregate before and after water treatment by chemiluminescent detection using a computer-controlled pyroreactor coupled to a nitrogen detector. A thermogram of nitrogen evolved versus pyroreactor temperature was measured.

Cylindrical briquets for the water susceptibility tests were prepared for various asphalt-aggregate mixtures. Water susceptibility tests (WST) involved water saturation and freeze-thaw cycling to failure.

Asphaltene settling tests (AST) were conducted. This test provides a sensitive measure of small changes in asphalt composition and to indicate the dispersibility of asphaltenes in n-hexane. The dispersion of asphaltenes in asphalt is important to asphalt-aggregate bonding and therefore to asphalt durability.

### 3.3.3 Test Results

#### 3.3.3.1 Thermograms

The temperature at which nitrogen compounds are desorbed from an aggregate surface can be used to evaluate the strength of nitrogen-aggregate interactions.

Pyridine-type nitrogen compounds in asphalts can be adsorbed on the aggregate surface to reduce the susceptibility of the resultant asphalt-aggregate mixture to the detrimental effects of moisture. For a given aggregate

more cyclohexyl-and triethylamines than pyridine were adsorbed on the aggregate surfaces.

Many aggregates that produced moisture-sensitive asphalt-aggregate mixtures show low nitrogen adsorption and/or higher than normal nitrogen displacement by water.

### 3.3.3.2 Water Susceptibility Tests

Two different silicate aggregates that had exhibited severe (A) and moderate (B) stripping problems were evaluated. Table 3.3.1 quantifies the effect of eight additives on water susceptibility tests using one asphalt and the two aggregates.

**TABLE 3.3.1 EFFECT OF EIGHT ADDITIVES ON WATER SUSCEPTIBILITY TEST RESULTS USING THE SAME ASPHALT ON TWO DIFFERENT AGGREGATES**

| Additive | W.S.T. Cycles to Failure | |
|---|---|---|
| | Aggregate A | Aggregate B |
| None (control) | 5 | 17 |
| Shale Oil: | | |
| -1% nitrogen conc. | 8 | 8 |
| -5% nitrogen conc. | 23 | 24 |
| Commercial Additives: | | |
| -Endulin AS Spec. | 8 | 12 |
| -Nea-3 | 4 | 20 |
| -Kling Beta XP-251 | 4 | 7 |
| -M-200 | 10 | 6 |
| -Pavebond AP Spec. | 37 | 8 |
| -Perma Tac | 44 | 8 |

### 3.3.3.3 Additives for Recycling Aged Asphalts

Important criteria for the recycling of asphaltic pavements are the restoration of pavement flexibility and durability. Restoration of these properties depends upon the ability of recycle agents to soften the aged asphalts and produce a compatible asphalt-recycle agent mixture that is relatively resistant to future oxidative hardening. Relatively large aging indices indicate rapid asphalt hardening and suggest possible early pavement failure from embrittlement and fracture. An increase in the asphaltene settling time (AST) from the addition of a recycle agent to an aged asphalt is regarded as indicative of the ability of the recycle agent to disperse polar components of the asphalt and improve asphalt-aggregate bonding.

Table 3.3.2 quantifies, in terms of asphaltene settling times (AST), the effect of different additives on two different asphalts. AST's are maximum for shale-oil-based additives. Similar results are shown in Table 3.3.3.

**TABLE 3.3.2 PROPERTIES FOR TWO ASPHALTS TREATED WITH DIFFERENT ADDITIVES**

| Asphalt | Additive Type | Additive Wt% | Viscosity, M P-as 25°C, 0.05/sec Before Aging | Viscosity, M P-as 25°C, 0.05/sec After Aging | Aging[1] Index | AST Min. | AST Final Vol, $cm^3$ |
|---|---|---|---|---|---|---|---|
| A | none | 0 | 4.27[2] | ---- | ---- | 74 | 10.9 |
| | shale oil distillate | 8.4 | 0.42 | 4.06 | 9.7 | 88 | 11.8 |
| | coal tar | 11.0 | 0.45 | 6.19 | 13.8 | 59 | 10.8 |
| | Paxole 1009 | 6.0 | 1.01 | 6.56 | 6.5 | 65 | 11.0 |
| B | none | 0 | 0.35[2] | ---- | ---- | 52 | 9.1 |
| | shale oil petrolene | 1.0 | ---- | ---- | ---- | 87 | 11.0 |
| | coal tar | 5.8 | 0.08 | 6.93 | 86.7 | 75 | 10.0 |
| | SRC-11 | 5.8 | 0.07 | 5.38 | 76.9 | 73 | 10.0 |
| | Dutrex 739 | 6.5 | 0.10 | 1.67 | 16.7 | 78 | 10.0 |

[1]Ratio of viscosity after laboratory aging to initial aged viscosity.
[2]Viscosity of recovered, aged asphalts before addition of recycle agents.

**TABLE 3.3.3 ASPHALTENE SETTLING TIME AND FINAL VOLUME OF PRECIPITATED ASPHALTENES MEASURED FOR AGED ASPHALT TREATED WITH SEVEN RECYCLE AGENTS**

| Recycle Agent[1] | AST Min. | AST Final Vol, $cm^3$ |
|---|---|---|
| none | 76.1 | 10.0 |
| shale oil: | | |
| -distillate | 56.8 | 9.3 |
| -nitrogen conc. | 93.5 | 11.0 |
| Cyclopave | 43.9 | 9.0 |
| SRC-11 | 49.4 | 9.1 |
| Paxole 1009 | 72.6 | 10.1 |
| Ashland 100 | 73.0 | 9.8 |
| Outrex 739 | 77.6 | 10.3 |

[1]One weight % additive based on asphalt sample.

### 3.3.4 Conclusions

The addition of polar nitrogen-containing additives derived from shale oil and from coal liquids improves the adsorption of asphalt to aggregate and enhances pavement flexibility and durability upon recycling.

## 3.4 Oxidation of Shale Oil Asphalts

Studies completed by Button et al. (1980) (Section 3.1) indicated that shale oil asphalts were susceptible to oxidative hardening. Petersen (1986) therefore investigated the possibility of modifying petroleum asphalts with shale oil residues. Petersen, through blending, hoped to minimize the adverse effects of oxidation seen in pure shale oil asphalts while retaining their unique properties of resistance to moisture damage in the blended product.

Blends of petroleum and shale oil asphalts containing up to 20% shale oil asphalt were subjected to laboratory air aging to simulate a 10 to 15 year old highway pavement. Rheological properties of the asphalts were determined and the chemical changes monitored using functional group analysis techniques based on selective chemical reactions and differential infrared spectroscopy. The moisture sensitivity of the asphalt-aggregate mixtures prepared from the blends were evaluated for water susceptibility.

The details of Petersen's investigations are published in a somewhat abbreviated form. Although the essence of the work is available, the publication does not present the work in the same detail as that referred to previously.

### 3.4.1 Materials

The materials used for the various tests consisted of a limestone aggregate and petroleum and shale oil asphalts. The petroleum asphalt was a Boscan petroleum asphalt, the shale oil asphalt was produced from Green River Formation shale oil to the same initial viscosity as the petroleum product.

### 3.4.2 Procedures

The petroleum asphalt was blended with 0, 5, 10 and 20% by weight of shale oil asphalt and the blends subjected to accelerated air aging. Aging indexes were assigned as a measure of the relative increases in viscosity on aging. The chemical changes which occur during oxidative aging were followed using functional group analysis techniques (Section 9.1.6) based on the combined use of selective chemical reactions and differential infrared spectroscopy.

Water susceptibility tests were used to test the moisture sensitivity of asphalt-aggregate mixtures containing the petroleum-shale oil asphalt blends. Highly permeable asphalt-aggregate briquets were suspended under water on a stress pedestal and subjected to repeated freeze-thaw cycles and warm-water-soak conditions until the briquet fails.

The results of the test procedures are listed in Table 3.4.1. The marginal increased oxidation of the blends, due to the increased reactivity of the shale oil component, is directly coupled to marked increases in resistance to water susceptibility.

**TABLE 3.4.1 AGING INDICES AND WATER SUSCEPTIBILITY TESTS ON SHALE OIL RESIDUE MODIFIED PETROLEUM ASPHALTS**

| % (wt.) of shale oil asphalt in asphalt blend | 0% | 5% | 10% | 20% |
|---|---|---|---|---|
| aging index | 300 | 323 | 333 | 380 |
| freeze-thaw cycles to failure | 7-13 | 25-31 | 26-37 | 58-62 |

### 3.4.3 Conclusions

Although neat shale oil residues are highly susceptible to oxidative hardening in air, blends with petroleum asphalt containing up to 20% shale oil residue show minimal increase in hardening rate upon aging compared with that of neat petroleum asphalt.

The beneficial effects of shale oil asphalts in improving the resistance of asphalt-aggregate mixtures to moisture damage was well noted in the blends.

## 4.0 NEW BRUNSWICK SHALE OIL COMPOSITION

The New Brunswick Research and Productivity Council, under contract to the New Brunswick Department of Commerce and Technology, has characterized shale oil produced from oil shales collected from the Albert Mines deposit in southeastern New Brunswick (Barua and Salib, 1985). The objectives of the study were, in part, to determine the physical and chemical characteristics of Albert Mines raw shale oil and to assess its suitability as a feedstock for the production of transportation fuels. As part of the study, the Albert Mines shale oil was compared to that of the Green River Formation of the Uinta Basin (Table 4.1). Properties for Athabascan tar sand bitumen and Saudi Arabian crude are listed herein for comparison purposes.

**TABLE 4.1 ELEMENTAL ANALYSIS OF ALBERT MINES AND GREEN RIVER FORMATION SHALE OIL, ATHABASCAN BITUMEN AND SAUDI ARABIAN CRUDE**

| | Albert Mines Shale Oil | | Green River Shale Oil | Athabascan Bitumen | Saudi Crude |
|---|---|---|---|---|---|
| | Indirect | Direct | | | |
| Carbon | 85.11 | 84.95 | 84.50 | n.a. | 85.00 |
| Hydrogen | 11.89 | 11.86 | 11.2 | 10.4 | 13.10 |
| Nitrogen | 1.0 | 1.02 | 1.96 | 0.6 | 0.10 |
| Oxygen | 0.77 | 0.75 | 1.60 | n.a. | 0.10 |
| Sulphur | 0.59 | 0.56 | 0.64 | 3.8 | 1.70 |
| Ash | 0.64 | 0.86 | 0.10 | 0.70 | 0.001 |
| H/C | 1.68 | 1.68 | 1.59 | n.a. | 1.85 |

n.a. - not available

The Albert Mines sample was retorted by two different modes. In the direct mode, process heat is generated inside the retort by the combustion of residual carbon. In the indirect mode, process heat is supplied from an external source by preheating recycle gas. No appreciable difference in the chemical properties of the resultant Albert Mines shale oil samples is evident from the data in Table 4.1.

The analytical results suggest that the Albert Mines shale oil is somewhat different from that of the Green River in terms of heteroatom content. Specifically, the nitrogen content of the Albert Mines samples is approximately half that of the Green River Formation shale oils. How this will affect the moisture susceptibility of an Albert Mines shale-oil based asphalt is unknown. Apparently, no such asphalts have been produced, or at least none have been reported, so no elemental analyses are available for comparison with the Green River shale oil asphalts.

The data from the Research and Productivity Council are corroborated at least in terms of their relative order of magnitude by those published by King (1963) for the Albert Mines and Green River oil shales (Table 4.2). King's figures, however, are for an "organic separate", that is, an extract of the organic portion of the oil shales concentrated by flotation techniques.

**TABLE 4.2 ELEMENTAL ANALYSES OF THE ORGANIC SEPARATE FROM THE ALBERT MINES AND GREEN RIVER FORMATION OIL SHALES**

| | Albert Mines Oil Shale Organic Conc. | Green River Oil Shale Organic Conc. |
|---|---|---|
| Carbon | 82.1 | 77.9 |
| Hydrogen | 10.7 | 9.7 |
| Nitrogen | 1.2 | 2.7 |
| Oxygen | 4.6 | 7.4 |
| Sulphur | 1.4 | 2.3 |
| Ash | 1.0 | 8.1 |
| H/C | 1.56 | 1.49 |

Altebaeumer (1984) isolated kerogen from samples of Albert Mines oil shales and analyzed the kerogen. The eleven samples yielded nitrogen ranging from 1.13 to 3.68 weight percent, with an average of 1.67 weight percent. Samples were collected and analyzed from all four lithologic units of the Frederick Brook facies; the dolomite marlstone zone appears to contain kerogen which has the highest nitrogen content (Table 4.3).

**TABLE 4.3 NITROGEN AND CARBON CONTENT OF ALBERT MINES DEPOSIT KEROGEN**

| Lithologic Unit | % N /Sample | % N Unit Av. | % C /Sample | % C Unit Av. |
|---|---|---|---|---|
| Upper Shale | 1.13 | | 77.17 | |
| Upper Shale | 1.30 | 1.22 | 63.25 | 70.21 |
| Albert Mines | 1.28 | | 70.60 | |
| Albert Mines | 1.44 | 1.36 | 74.72 | 72.66 |
| Clay | 1.48 | | 71.28 | |
| Clay | 1.23 | 1.36 | 56.90 | 64.09 |
| Dolomite | 1.59 | | 66.09 | |
| Dolomite | 3.68 | | 74.30 | |
| Dolomite | 1.95 | | 56.35 | |
| Dolomite | 1.66 | | 59.72 | |
| Dolomite | 1.62 | 2.10 | 71.21 | 65.53 |

Several studies have reported the nitrogen content of Albert Mines oil shale and shale oil (St. Peter, 1984). Comparing the nitrogen content of anything but similarly retorted oil shale and/or similarly produced asphalt could, however, be misleading. King's and Altebaeumer's analyses refer to the nitrogen content of the hydrocarbon constituent of the oil shales; the variability in quality and quantity of the inorganic constituents are thus negated. R.P.C.'s figures result from a product produced by a retorting process that has "close similarities" with the Paraho process; it is not, however, exactly the same. This difference could introduce an unknown into comparisons between the retorted Albert Mines and Green River Formation oil shales but the figures quoted are the best presently available.

No information exists on the chemical nature of the nitrogen in the Albert Mines shale oils. Analyses are quoted in total weight percent nitrogen only, the nitrogen compounds are not identified.

Barua and Salib indicate that the Albert Mines shale oil has a low asphaltene content. Asphaltenes are polyaromatic compounds with high carbon to hydrogen ratios which are a major constituent of asphalts. This feature of Albert Mines shale oils, while beneficial when one is interested in producing "light-end" hydrocarbons, could be detrimental to the production of "heavy-end" products such as asphalt. The dependence of the "heavy-ends" or residual content of a shale oil upon the nature of the retorting process is not addressed herein nor is the question of the preferred process of asphalt production from Albert Mines oil shale. Those questions are subjects warranting further study.

## 5.0 LOCAL ASPHALT PRODUCTION AND CONSUMPTION

In order to fully evaluate the potential for the utilization of New Brunswick shale oil as an asphalt feedstock the structure of the existing asphalt markets in Atlantic Canada was examined. To this end a brief summary of the nature and magnitude of the production and consumption capacities of asphalt in Atlantic Canada has been prepared. Several sources of information were utilized to acquire the necessary data. They included the departments of transportation in the four provinces, discussions with private industry and published information.

### 5.1 Production

Two producers of asphalt exist in Atlantic Canada, Imperial Oil in Dartmouth, Nova Scotia and Irving Oil in Saint John, New Brunswick. Imperial's capacity is 717 tonnes/day and Irving's is 2,118 tonnes/day. These two refineries account for 25% and 75%, respectively, of the region's asphalt production capacity and for 5% and 15%, respectively, of Canada's total asphalt production capacity. The Irving refinery has the second largest asphalt production capacity in the country after Petro-Canada's Montreal East refinery. The Irving facility, at 37,760 $m^3$/day, has the largest crude oil refining capacity of any single refinery in the country, exceeding its nearest rival, Imperial's Edmonton, Alberta refinery by 11,560 $m^3$/day.

Table 5.1 lists the asphalt production capacities of the individual refineries in Atlantic Canada and Quebec and the total capacities of all refineries in Ontario and Western Canada. The proportion of the regional and national capacity contributed by each refinery and region is also quoted.

**TABLE 5.1 CANADIAN ASPHALT PRODUCTION CAPACITY**

| | | Tonnes/Day | % of Regional Total | % of National Total |
|---|---|---|---|---|
| **Atlantic Canada:** | | | | |
| Newfoundland | | | | |
| Nfld. Energy | Come-by-Chance | ------ | | |
| Nova Scotia: | | | | |
| ESSO | Dartmouth | 717 | 25% | 5% |
| Texaco | Halifax | ------ | | |
| New Brunswick: | | | | |
| Irving | Saint John | 2,118 | 75% | 15% |
| Regional Total | | 2,835 | 100% | 20% |
| **Central Canada:** | | | | |
| Quebec: | | | | |
| Kemtex (Lavalin) | Montreal | ------ | | |
| Petro-Can | Montreal | 2,438 | 39% | 17% |
| Shell | Montreal | 1,311 | 22% | 10% |
| Ultramar* | Levis | ------ | | |
| Ontario: | 2,438 | 39% | 17% | |
| Regional Total | | 6,187 | 100% | 44% |
| Western Canada | | 4,948 | 100% | 36% |
| National Total | | 13,970 | | 100% |

Source: Oilweek, MacLean-Hunter Ltd., Vol. 39, No. 22

*: Reported as having asphalt production by T. Gorman of N.B.D.O.O.T. and J. McMackin of Atlantic Colas Ltd.

## 5.2 Consumption

Information for 1987 on the consumption of asphalt in Atlantic Canada was sought from the appropriate representatives of the four provincial Departments of Transportation. The information for New Brunswick was gained through a personal interview, the other three Departments were contacted by telephone and their attitude towards the receipt of a written questionnaire sought. All three provinces agreed to respond to a written questionnaire although ultimately only Newfoundland supplied information. In order to obtain input from the private sector, an interview was held with a representative of Atlantic Colas Ltd., a manufacturer and applicator of asphalt emulsions in Atlantic Canada.

On the basis of the information obtained, it is possible to make several specific statements concerning the structure and magnitude of asphalt markets in New Brunswick and Newfoundland. Utilizing the New Brunswick and Newfoundland data in conjunction with statistics detailing the population and the number of kilometres of paved roads in the four provinces it was possible to make several basic assumptions concerning the asphalt markets in Nova Scotia and Prince Edward Island.

### 5.2.1 New Brunswick

In New Brunswick, in 1987, all asphalt used in asphaltic concretes for provincial government contracts was supplied to the various paving contractors by the Department of Transportation. The asphalt cement was supplied to the Department by Irving Oil at an average cost of $289 per tonne F.O.B., Saint John, New Brunswick. The Department

purchased approximately 26,600 tonnes of asphalt cement in 1987 worth approximately $7,700,000. No figures, however, were obtained for the quantity of asphalt cement used by municipalities or the private sector. Asphalt cement utilization by these sectors in Newfoundland in 1987 and the relative populations of Newfoundland and New Brunswick provides a basis for estimating asphalt consumption by these sectors in New Brunswick. The Newfoundland consumption of asphalt by municipalities and the private sector was 22,000 tonnes in 1987 and its population is 79% of that of New Brunswick. Therefore, the consumption of asphalt cement in New Brunswick by non-provincial government sectors has been estimated at 28,000 tonnes, worth approximately $8,000,000.

The use of emulsified asphalts by all sectors contributes significantly to asphalt utilization in New Brunswick. Four producers of these products now exist in the province, Atlantic Colas in Saint John, Coke Asphalt in Moncton, McAsphalt in Perth and ACE Asphalt in Oromocto. In 1987, approximately 8,500,000 litres of emulsified asphaltic products were used in the province. These products averaged approximately 65% asphalt, for a total of approximately 5,525,000 litres of asphalt. This equates to 5,660 tonnes of asphalt worth approximately $1,636,000.

A total of these various figures indicates that the consumption of asphalt cement used in New Brunswick in 1987 amounted to approximately 60,260 tonnes worth approximately $17,400,000.

### 5.2.2 Newfoundland

In Newfoundland in 1987, all asphalt used in asphaltic concretes for provincial government contracts was supplied by Newfoundland Hardwoods, a provincial crown corporation. The asphalt cement was supplied to Newfoundland Hardwoods by Imperial Oil of Dartmouth, Nova Scotia. The average cost to the provincial Department of Transportation was approximately $285 per tonne F.O.B., Clarenville, Newfoundland. In 1988, the department's policy changed and asphalt cements are now purchased by the various paving contractors directly from the supplier(s) of their choice. In 1987, approximately 32,000 tonnes of asphalt cement worth approximately $9,100,000 was supplied to the Newfoundland highway system. During the same year approximately 22,000 tonnes of asphalt cement were used by municipalities and the private sector for the production of asphaltic concretes. This asphalt was worth approximately $6,300,000.

The use of emulsified asphalts by all sectors in Newfoundland is significantly smaller than that in New Brunswick. In 1987, these products were manufactured by Atlantic Colas at the Newfoundland Hardwoods plant in Clarenville. A total of 40,000 litres of emulsion were manufactured using approximately 26,000 litres of asphalt. This equates to approximately 26 tonnes of asphalt worth approximately $7,410,000.

The total of these various figures indicates that the consumption of asphalt cement used in Newfoundland in 1987 amounted to approximately 54,000 tonnes worth approximately $15,390,000.

### 5.2.3 Nova Scotia and Prince Edward Island

The lack of hard data for the provinces of Nova Scotia and Prince Edward Island has necessitated that the size of these markets for asphalts must be estimated based upon the data from New Brunswick and Newfoundland. The comparisons have been made based upon the total number of kilometres of paved roads in each province. Table 5.2 presents the length of paved roads under provincial and municipal jurisdiction in the Atlantic Provinces, Quebec, Ontario and Western Canada. The figures have been adjusted to the equivalent of a two-lane highway.

Nova Scotia has approximately the same quantity of paved roads as New Brunswick whereas Prince Edward Island has only 25% of New Brunswick's total. New Brunswick has been used for comparison purposes as opposed to Newfoundland since it is assumed that weather conditions in New Brunswick and Prince Edward Island are similar and therefore asphalt consumption for road maintenance would be similar. Based upon these assumptions, Nova Scotia's consumption of asphalt approximates 60,260 tonnes per year and is worth approximately $17,400,000 and that Prince Edward Island's consumption approximates 15,000 tonnes and is worth approximately $4,350,000.

The quantity of asphalt consumed and its value in the four Atlantic Provinces is listed on Table 5.3. In 1987, the region consumed a total of approximately 189,520 tonnes of asphalt valued at $54,540,000.

**TABLE 5.2 THE LENGTH OF THE CANADIAN ROAD NETWORK (Two-Lane Equivalent km)**

| | Provincial Jurisdiction | Municipal Jurisdiction | Total | % of National Total |
|---|---|---|---|---|
| Atlantic Canada: | | | | |
| Newfoundland | 5,568 | 2,438 | 8,006 | 2.1% |
| Nova Scotia | 12,428 | 2,072 | 14,500 | 3.7% |
| P.E.I. | 3,350 | 184 | 3,534 | 0.1% |
| New Brunswick | 11,800 | 2,550 | 14,350 | 3.7% |
| Regional Total | 33,146 | 7,244 | 40,390 | 9.6% |
| Central Canada: | | | | |
| Quebec | 38,600 | 30,000 | 68,600 | 17.8% |
| Ontario | 23,233 | 68,208 | 91,441 | 23.7% |
| Regional Total | 61,833 | 98,208 | 160,041 | 41.5% |
| Western Canada*: | 136,021 | 53,042 | 189,063 | 48.9% |
| TOTAL | 231,000 | 158,494 | 389,494 | 100% |

*: Includes N.W.T. and Yukon

Source: Roadway Infrastructure Study, Roads and Transportation Association of Canada, 1987

**TABLE 5.3 CONSUMPTION OF ASPHALT IN ATLANTIC CANADA**

| | Quantity (tonnes) | Value (Cdn$) |
|---|---|---|
| Newfoundland | 54,000 | 15,390,000 |
| Nova Scotia | 60,260 | 17,400,000 |
| Prince Edward Island | 15,000 | 4,350,000 |
| New Brunswick | 60,260 | 17,400,000 |
| TOTAL | 189,520 | 54,540,000 |

## 5.3 Market Trends and Potential

The process of acquiring the data necessary to quantify asphalt markets in Atlantic Canada also yielded general information on the state of the asphalt market in the region, particularly on its developing trends and potential.

The asphalts laid on new highways are designed for a 15 year life expectancy. Throughout the region this term is now being approached or has already been exceeded by several of its major highways. In New Brunswick a completely new Trans-Canada Highway is being actively considered. In Newfoundland a Federal and Provincial agreement (Newfoundland and Labrador Transportation Initiative Agreement) calls for the spending of $405,000,000 to upgrade the Trans-Canada Highway and over $300,000,000 to construct and/or improve secondary roads.

The literature and regional highway officials note increased wear and rutting of asphalt pavements. This phenomena is attributed to one or more of several causes by various sources. The causes include higher volumes and unit weights for truck traffic, higher tire inflation pressures, use of radial tires on trucks (in combination with the former two causes), insufficient road bases for current use and load levels and deteriorating asphalt properties. There is considerable discussion in the asphalt industry concerning asphalt quality. Whether the problem is with the actual asphalts or with the adequacy of specifications which are used to determine the suitability of asphalt cements in asphaltic concretes is uncertain. Currently, specifications for asphalt cements concentrate on physical properties, no chemical parameters are taken into account. Asphalt

chemistry obviously affects the properties of asphalts and many believe should be taken into account in the process of testing and defining of specifications. Tangible evidence of the concern for these various problems, not the least of which is the aging of North America's highway system, is the implementation in the U.S. of the Strategic Highway Research Program (SHRP) by the National Academy of Science and the National Research Council. Various interested government agencies in Canada, including provincial departments of transportation and specifically the New Brunswick Department of Transportation, are participating in this initiative.

The quality, particularly in terms of durability, of asphalt cements is obviously an industry wide concern. Similarly, the deteriorating condition of the region's and in fact of the continent's highway system must be addressed and rectified over the next one to two decades. The combination of these two factors places any asphalt or asphaltic product which offers enhanced durability characteristics in an advantageous position. It therefore appears that if in fact shale oil asphalts possess enhanced durability characteristics their development in the near future is now worthy of consideration in order to take advantage of the apparent developing need for such a product.

In terms of the actual state of asphalt supply in the region and the country, Atlantic Canada and New Brunswick in particular has no shortage of supply or at least of capacity to supply. Table 5.4 provides a comparison of the regional distribution of national asphalt production capacity and market demand, in terms of the distribution of the national road network. Atlantic Canada's asphalt production capacity, due for the most part to the Irving Oil refinery's

capacity in Saint John, exceeds its local market demand to a greater extent that any other province or region. Quebec displays figures of approximately the same order of magnitude. As a result, Atlantic Canada's and in particular New Brunswick's surplus can be moved into Newfoundland, west into Central and Western Canada, south into the United States and possibly offshore.

The surplus in local production capacity of asphalt indicates that any new product must compete primarily on the basis of quality, it must out-perform the competition. The existing surplus in capacity to supply suggests that competitive pricing strategies can be adopted by existing suppliers to prevent market penetration by a new product.

**TABLE 5.4 COMPARISON OF ASPHALT CAPACITY AND THE LENGTH OF THE ROAD NETWORK BY REGION**

| | % of national asphalt production capacity | % of national road network | difference (cap.-roads) |
|---|---|---|---|
| Atlantic Canada: | | | |
| Newfoundland | -- | 2.1% | -2.1% |
| Nova Scotia | 5% | 3.7% | +1.3% |
| P.E.I. | -- | 0.1% | -0.1% |
| New Brunswick | 15% | 3.7% | +11.3% |
| Regional Total | 20% | 9.6% | +10.4% |
| Central Canada: | | | |
| Quebec | 27% | 17.8% | +9.2% |
| Ontario | 17% | 23.7% | -6.7% |
| Regional Total | 44% | 41.5% | +2.5% |
| Western Canada | 36% | 48.9% | -12.9% |

## 6.0 CONCLUSIONS

Asphalt produced from shale oil retorted from the Green River Formation in the western United States exhibits superior resistance to damage by moisture. Evidence indicates that basic, probably pyridinic, nitrogen compounds are responsible for the observed increased moisture resistance of shale-oil-derived asphaltic concretes. As well, it has been found that the addition of nitrogen-bearing additives derived from shale oil and from coal liquids enhance pavement flexibility and durability upon recycling.

Green River Formation shale oil asphalts have been found to be susceptible to oxidative hardening, a feature detrimental to pavement durability. Blends of petroleum asphalts and up to 20% shale oil asphalt, however, show no abnormal susceptibility to oxidative hardening but do exhibit improved resistance to moisture damage.

Shale oil derived from the Albert Formation of New Brunswick contain approximately half the total nitrogen content of the Green River Formation shale oils. No information, however, exists indicating the relative content of the various types of nitrogen compounds in the New Brunswick oil shales. This factor is important since it appears that pyridinic nitrogen compounds are responsible for the observed enhanced moisture resistance of shale-oil-derived asphaltic concretes. It is conceivable that the concentration of these types of nitrogen compounds in New Brunswick shale oils may be such so as to impact positively upon durability characteristics, similar to that seen in shale oil asphalts derived from the Green River Formation.

The use of New Brunswick shale oil as a feed stock for the production of asphalt to be blended with conventional petroleum asphalts or for the production of an asphalt recycling agent appears to be worthy of further consideration. To this end a program of further work is recommended. A suitably sized sample of New Brunswick shale oil must be acquired, analyzed and distilled to yield a sample of asphalt. The shale oil asphalt can then be blended and the appropriate tests conducted to determine whether New Brunswick shale oil asphalts possess the enhanced durability characteristics of the Green River Formation shale oil asphalts. An outline of the recommended work program and budget follow in Section 7.0.

## 7.0 RECOMMENDATIONS

In order to determine whether New Brunswick shale oils offer any potential as a source of asphalts having superior durability it is necessary to produce samples of both shale oil and shale oil asphalt for testing purposes. The shale oil must be fully characterized and the shale oil asphalts not only characterized but also used in the preparation of samples of asphaltic concretes and tested in a manner similar to the studies completed on the western U.S. shale oil asphalts.

### 7.1 Work Program

Initially a sample of shale oil is required for analysis and from which to produce the asphalt sample. The apparent availability of the shale oil to be retorted from the New Brunswick oil shale samples shipped to Brazil by Canadian Occidental Petroleum Ltd. in October, 1988 will alleviate the need to have to mount a special sampling and retorting program. Discussion with officials of Canadian Occidental (Dr. E. Yildirim) and Stone and Webster Engineering Corp. (E.M. Piper), the latter representing Petroleo Brasilerio S.A. owners and operators of the Petrosix oil shale retort, indicate that sufficient quantities of shale oil can be returned to New Brunswick to fulfill the requirements of this program.

At the outset it would be useful and advisable to have sufficient analyses of the oil shale available to permit its comparison with the Green River Formation oil shale. Of particular interest is the nitrogen content and the content of pyridine-type homologs in the shale oil.

Discussions concerning the production and testing of the shale oil asphalt have been undertaken with Dr. M.R. Wilson of CANMET's Energy Research Laboratories in Ottawa. As a result of those discussions the following work is proposed.

New Brunswick shale oil would be distilled to penetrations of 85-100 and blended with an appropriate conventional asphalt from Atlantic Canada to obtain blends of 5%, 10%, 25% and 50%. The properties of these blends together with neat shale oil and conventional asphalts would be investigated. These efforts would constitute Phase I of the work proposed. Depending upon the generation of positive results, Phase II could be instituted. Phase II would involve the preparation of asphaltic concrete samples and their testing in a manner similar to which the Green River Formation oil shale asphalts have been subjected.

**Phase I - Laboratory Evaluation**

**Task I - Acquisition of Samples**

a) shale oil: 5-10 gallons of sample to yield 1 gallon of asphaltic residue

b) conventional asphalt: 2 gallons of an appropriate conventional asphalt

c) aggregate: 5 gallons of an appropriate aggregate for preparation of briquets for freeze-thaw tests

Task 2 - Literature Review and Visits

A literature search on information relevant to the utilization of shale oil fractions in asphalt has been completed and a full review of its content is required by laboratory staff. Detailed in-person discussions with those active in the field at the Western Research Institute in Laramie, Wyoming and the New Paraho Corporation in Colorado are necessary prior to actual testing. Their experience and knowledge in the field must be accessed prior to implementing a testing program.

Task 3 - Distillation and Blending

The shale oil shall be distilled to produce 1 gallon of 85-100 penetration asphalt or other grade (either penetration or viscosity graded) if necessary. The initial distillation shall be atmospheric to about 200°C and then under reduced pressure to avoid excessive temperatures.

Four blends containing 5%, 10%, 25%, and 50% of shale oil asphalt with the conventional asphalt sample shall be prepared in adequate amounts for subsequent tasks.

Task 4 - Routine Tests (AASHTO and/or ASTM)

The following tests shall be performed on the 4 blends, the shale oil asphalt and conventional asphalt samples:

Viscosities at 25°, 60° and 135°C
Penetrations at 25° and 4°C
Softening Points
Specific Gravity at 25°C
Ductility at 25°C

| | | |
|---|---|---|
| Solubility ($CHCl_3$: $CCl_2$) | | |
| Flash + Fire Points | | |
| Spot Test | | |
| Thin-Film Oven Test | - | penetration of residue at 25°C |
| | - | ductility of residue at 25°C |
| | - | viscosity of residue at 60°C |
| | - | loss of material during test |
| Hardening Index | - | to be calculated using TFOT results (at least initially) |
| Penetration Index | - | to be calculated from penetration values at different temperatures |
| Elemental Analyses | - | carbon, hydrogen, nitrogen, sulphur and oxygen; vanadium, nickel, iron and other metals. |

**Task 5 - Non-Routine Tests**

**Freezing and Thawing Tests**

Water susceptibility tests shall be made according to the method developed by the Western Research Institute in Laramie, Wyoming (Plancher et. al. 1982). Briquets shall be made of the six asphaltic samples that are mixed with aggregate for subjecting to freezing and thawing cycles. These briquets shall be prepared using a narrow particle size range of crushed and sieved aggregate with appropriate amounts of asphaltic materials (usually 5%). These briquets after being fixed to pedestals shall be subjected to freezing and thawing cycles in water until cracks begin to appear. The number of cycles before cracking is a measure of resistance to stripping of asphalt from aggregate by water during freezing and thawing.

Asphaltene Settling Tests

These tests shall be carried out on the six asphaltic samples also according to a method developed by the Western Research Institute.

Note: The value of this test is controversial, but is claimed to give a measure of the peptizing power of asphalt systems for asphaltenes which can be related to asphalt longevities. At this time, this aspect is being studied by the Alberta Research Council for the Energy Research Laboratories, as a part of a contract. The outcome of this work should be available shortly and a decision on whether or not to carry out this test can then be made.

Task 6 - Characterization

The shale oil asphalt and the conventional asphalts shall be separated into saturate, naphthene-aromatic, polar-aromatic and asphaltene fractions according to ASTM procedure 4124. In addition the asphaltenes of all blends shall be determined. Infra-red spectra shall be obtained of all of these fractions and the significant peaks shall be interpreted in terms of functional groups and hydrocarbon structures (1, 3, 4). The range of basicity levels for the shale oil asphalt and the conventional asphalt should be determined by non-aqueous titration. (The basic nitrogen compounds are probably pyridinic but some of the more basic nitrogen groups such as amines might also be present). The pyrollic (non-basic) nitrogen groups shall be quantatively determined by infra-red spectrometry.

Task 7 - Reporting

Monthly progress reports shall be prepared. In these reports all the data and findings obtained as well as significant observations shall be reported. Where appropriate, brief discussions shall be included. If trips have been made then these shall be satisfactorily reported. Also any significant new articles found in the literature or newly obtained information relevant to this work shall be included in the reports.

A final detailed report shall be prepared that includes all the data/information generated.

7.2 Budget

For the purposes of budget preparation it has been assumed that no oil shale sampling or shale oil retorting will be required. The apparent availability of the shale oil to be produced by the Petrosix process deletes the need to budget for the retorting of a sample of New Brunswick shale oil. The costing is based on a submission prepared by CANMET, no competitive submissions were sought.

| | | | | |
|---|---|---|---|---|
| Task 1 | - | if samples are provided then no charges will be applied | | |
| Task 2 | - | Literature Review | 30 hrs. | |
| | | Visits | 75 hrs. | |
| | | | 105 hrs.= | $12,070 |
| Task 3 | - | Distillation | 37.5 hrs. | |
| | | Blending | 7.5 hrs. | |
| | | | 45 hrs.= | $5,173 |
| Task 4 | - | Routine Testing | = | $6,500 |

| | | | | |
|---|---|---|---|---|
| Task 5 | - | Non-Routine Tests | | |
| | | a) freeze-thaw | 85 hrs. | |
| | | b) asphaltene settling | 25 hrs. | |
| | | | 110 hrs. | = $ 12,646 |
| Task 6 | - | Characterization | 50 hrs. | = $ 5,748 |
| Task 7 | - | Reporting | 60 hrs. | = $ 6,308 |
| | | Total | | = $ 48,445 |

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# 9.0 APPENDICES

## 9.1 Standard Test Procedures

### 9.1.1 Flash and Fire Points by Cleveland Open Cup

AASHTO Designations: T48 (presented below) .
ASTM Designation: D92

Flash and fire point tests serve as evidence of the fractionation control of the volatiles in asphalts. They are of particular interest for the transportation, handling, heating and application of asphalts.

The test consists of filling a test cup to a specified level with a sample of the material to be tested. The temperature of the sample is increased rapidly at first and then at a slow constant rate as the anticipated flash point is approached. At specified intervals a small test flame is passed across the cup. The lowest temperature at which application of the test flame causes the vapours above the surface of the liquid to ignite is taken as the flash point. To determine the fire point, the test is continued until the application of the test flame causes the sample to ignite and burn for of least 5 seconds.

### 9.1.2 Indirect Tension Test for Resilient Modulus of Bituminous Mixtures

ASTM Designations: 04123

This procedure covers the preparing and testing of laboratory-fabricated or field-recovered cores of bituminous mixtures to determine resilient modulus values using the repeated-load indirect tension test. A series of tests are conducted under prescribed temperatures, loads, loading frequencies and load durations.

Compressive loads are applied vertically in the vertical diametral plane of a cylindrical specimen of asphaltic concrete. The resulting horizontal deformation of the specimen is measured and, with an assumed Poissons ratio, is used to calculate a resilient modulus. A resilient Poissons ratio can also be calculated using the measured recoverable vertical and horizontal deformations. Two resilient modulus values result. The instantaneous resilient modulus is calculated from the recoverable deformation that occurs instantaneously during the unloading portion of one cycle. The total resilient modulus is calculated using the total recoverable deformation which includes both the instantaneous recoverable and the time-dependent continuing recoverable deformation during the unloading and rest-period portion of one-cycle.

The values of resilient modulus can be used to evaluate the relative quality of materials as well as to generate input for pavement design or pavement evaluation and analysis. The test can be used to study effects of temperature, loading rate, rest periods etc. Since the procedure is nondestructive tests can be repeated on a

specimen to evaluate conditioning as with temperature or moisture.

The procedure can also be used to determine tensile strength where sufficient load is applied to the specimen to cause it to fail.

### 9.1.3 Penetration of Bituminous Materials

AASHTO Designation: T49 (presented below)
ASTM Designation: D5

The penetration of a bituminous material is the distance in tenths of a millimetre that a standard needle penetrates vertically into a sample of the material under fixed conditions of temperature, load and time. The sample is melted and cooled under controlled conditions.

Very hard asphalts have zero penetration while the softer ones range up to 250 (25 mm).

Penetration index - a numerical expression of the relationship between softening point (Section 9.1.7) and penetration (Section 9.1.3) as determined from a monograph published by Rostler (1965); the penetration index is directly proportional to softening point and penetration.

### 9.1.4 Preparation of Test Specimens of Bituminous Mixtures by Means of Gyratory Shear Compactor

ASTM Designation: D4013

This procedure covers the preparation of 10 cm diameter test specimens of bituminous mixtures containing minus 22.4 mm aggregate. The procedure employs gyratory-shearing action of the mixture at low initial pressures, allowing orientation of the aggregate particles to aid compaction and then nongyratory compression at high pressure for consolidation and shaping.

The specimens are compacted to simulate the density, aggregate degradation and structural characteristics possible in the actual road surface when proper construction procedure is used in the placement of the material. The specimens may be used to determine stability, density, strength, water susceptibility, etc. of bituminous mixtures.

### 9.1.5 Resistance to Plastic Flow of Bituminous Mixtures using Marshall Apparatus

ASTM Designation: D1559

This procedure covers the measurement of the resistance to plastic flow of cylindrical specimens of bituminous paving mixtures loaded on the lateral surface by means of the Marshall apparatus. The method is for use with mixtures containing a bituminous binder and aggregate up to 25.4 mm. Specimens prepared in accordance with the method are tested for maximum load and flow. Density and void properties may also be determined. The procedure can be used to obtain maximum load and flow for bituminous paving specimens cored from pavements or prepared by other methods. These results, however, may differ from valves obtained on specimens prepared by this method.

The asphalt mixture to be tested is prepared as prescribed by the procedure and placed in a standard mold assembly (101.6 mm in diameter by 76.2 mm in height). Compaction occurs by a prescribed number of measured free fall vertical blows of a hammer on both ends of the mold assembly. The extracted molded sample is then used for various tests including measurement of resistance to plastic flow.

### 9.1.6 Separation of Asphalt into Four Fractions

ASTM Designation: D4124

This procedure covers the separation of four defined fractions from petroleum asphalts. The four fractions are defined as saturates, naphthene aromatics, polar aromatics and $_nC_7$ asphaltenes. The procedure can also be used to isolate saturates, naphthene aromatics and polar aromatics from distillate products such as vacuum gas oils, lubricating oils and cycle stocks. These distillate products usually do not contain asphaltenes.

Analysis of the fractions can be used to evaluate asphalt composition. For example, one can compare the ratios of the fractions with other asphalt systems to evaluate processing and aging parameters that relate to performance properties of the asphalt.

### 9.1.7 Softening Point of Asphalt

AASHTO Designation: T53 (presented below)
ASTM Designation: D2398

Asphalt and tar, including tar pitches, do not change from the solid state to the liquid state at any definite temperature, but gradually become softer and less viscous as the temperature rises. Softening point is useful in the classification of certain asphalts and tars, including tar pitches and is indicative of the tendency of the material to flow at elevated temperatures encountered in service.

A steel ball of specified weight is placed upon a disk of sample contained within a horizontal, shouldered, metal ring of specified dimensions. The assembly is heated in an ethylene glycol bath at a uniform, prescribed rate and the softening point taken as the temperature at which the sample becomes soft enough to allow the ball, enveloped in the sample material, to fall a distance of 25.4 mm.

### 9.1.8 Spot Test

AASHTO Designation: T102

This test is primarily a test to distinguish the differences in heterogeneity between straight-run and cracked asphalts. Straight-run asphalts are exposed to high temperatures for only very short periods of time and are therefore not decomposed and hydrocarbons which are difficult to disperse are not formed. Consequently the asphalt is soluble or dispersible in naphtha yielding a "negative" spot test. Highly cracked residues, those which have been exposed to extremely high temperatures, contain hydrocarbons having a high ratio of carbon to hydrogen, small portions of which are only partly dispersible in naphtha. The residues noted in such tests constitute a "positive" spot test.

### 9.1.9 Thin-Film Oven Test

AASHTO Designations: T179 (presented below)
ASTM Designations: D1754

This test is used to determine the effect of heat and air on asphalt. A 3.2 mm film of asphaltic material is heated in an oven for 5 hours at 163°C. The amount of hardening is evaluated from the reduction in penetration, expressed as the percentage of the original value. Ductility or any other property of asphaltic residue may also be evaluated. An optional procedure for determining the loss or gain in sample mass is also included.

The test indicates approximate susceptibility to hardening and loss of ductility of asphalt cements during mixing.

### 9.1.10 Viscosity of Asphalts

AASHTO Designation: T202 (presented below)
ASTM Designation: D2171

The absolute viscosity of asphalt is determined by measuring the time a fixed volume of the liquid to be drawn up through a capillary tube by means of vacuum, under closely controlled conditions of vacuum and temperature. The absolute viscosity in poises is calculated by multiplying flow time in seconds by the viscometer calibration factor.

### 9.1.11 Viscosity Graded Asphalt Cements

AASHTO Designation: M226

Determination of absolute viscosity of asphalts by AASHTO T202 (ASTM D2171) permits the grading of the asphalt based upon its viscosity. The maximum limits for viscosity for the various grades of asphalt are as follows:

| Viscosity Grades | Maximum Viscosity poises (60°C) |
|---|---|
| AC-2.5 | 1,000 |
| AC-5 | 2,000 |
| AC-10 | 4,000 |
| AC-20 | 8,000 |
| AC-40 | 16,000 |